PATENT APPLICATION OF

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ENTITLED

METHOD AND APPARATUS USING A CIRCUIT MODEL
TO EVALUATE CELL/BATTERY PARAMETERS

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METHOD AND APPARATUS USING A CIRCUIT MODEL
TO EVALUATE CELL/BATTERY PARAMETERS

This is a Continuation-In-Part of patent application Serial No. **09/940,684** filed August 27, 2001 which is a Divisional of patent application Serial No. **09/388,501** filed September 1, 1999, which issued as U.S. Patent **6,313,607** on November 6, 2001 and also claims priority to U.S. provisional application Serial No. **60/299,876** filed June 21, 2001, the contents of which are hereby incorporated by reference in their entirety.

BACKGROUND OF THE INVENTION

"Total storage capacity" (**TSC**), "absolute stored charge" (**ASC**), "state-of-charge" (**SOC**), "absolute cranking current" (**ACC**), "fully charged cranking current" (**FCCC**) and "state-of-health" (**SOH**) are important performance parameters of an electrochemical cell/battery. These six parameters are assumed herein to have the following definitions:

- "Total storage capacity" (**TSC**) denotes the total amount of charge that a fully charged battery can supply under specified discharge conditions. **TSC** is usually expressed in ampere-hours or in reserve capacity minutes.

- "Absolute stored charge" (**ASC**) -- also expressed in ampere-hours or reserve capacity minutes -- denotes the amount of charge that a battery can supply in its current charge state. As a battery is discharged, its **ASC** decreases -- much like the level of liquid in a fuel tank.

- "State-of-charge" (**SOC**), or "relative stored charge", is the ratio of a battery's **ASC** to its **TSC** -- generally expressed as a percentage. A battery's **SOC** indicates whether charging is advisable and identifies the point at which charging should be discontinued.

- "Absolute cranking current" (**ACC**) denotes the high-rate discharge current in amperes that a battery can sustain at a specified voltage for a specified time in its present charge state. As a battery discharges, its **ACC** decreases.

- "Fully charged cranking current" (**FCCC**) denotes the value that the **ACC** would assume if the battery were fully charged.

- "State-of-health" (**SOH**) describes a battery's full charge capability, either its **TSC** or its **FCCC**, vis-à-vis its rated specifications. **SOH** identifies the point at which battery replacement is advisable.

Both **ASC** and **TSC** have traditionally been measured by performing timed-discharge tests on batteries that are partially or fully charged, respectively. Because of the time and expense involved in performing complete discharge tests, other techniques for determining **ASC** and **TSC** have been proposed. In U.S. Patent **6,255,801,** Chalasani claims to determine battery capacity from observations of the coup de fouet effect. O'Sullivan, in U.S. Patent **6,211,654,** discloses a method for predicting battery capacity from the discharge characteristics over a relatively short time period at the beginning of a full discharge.

Techniques employing time-varying signals have also been proposed. Sharaf, in U.S. Patent **3,808,522,** purportedly determines the ampere-hour capacity of a lead-acid battery from ac measurements of its internal resistance. Yang, in U.S. Patent **5,126,675,** also uses single-frequency internal resistance measurements to predict battery capacity. Muramatsu reports in U.S. Patent **4,678,998** that he can determine both the remaining amp-hour capacity and the remaining service life of a battery from measurements of the magnitude of the ac impedance at two different frequencies. Fang, in U.S. Patent **5,241,275,** teaches a method for determining remaining capacity from complex impedance measured at two or three frequencies in the range from **0.001** to **1.0** Hz. Hampson, et al., in U.K. Patent Application **GB 2,175,700A,** report determining battery capacity from the frequency of the maximum value of capacitive reactance in the "impedance characteristic curve". Yoon et al., in U.S. Patents **6,208,147** and **6,160,382,** claim that a battery's capacity can be found by analyzing the complete impedance spectrum over a wide frequency range. Presumably, any of these techniques, if effective, could also be used to determine **SOH** by comparing the **TSC** thus determined with a rated value.

Champlin, in U.S. Patent **5,140,269,** shows that the percent capacity of a standby battery -- and hence its **SOH** -- can be determined from its ac conductance measured at a single frequency if the ac conductance of a reference, fully charged, identically constructed, new battery is known. This method, although quite

effective, requires that such ac conductance data be available, *apriori*.

"Absolute cranking current" (**ACC**) and "fully charged cranking current" (**FCCC**) have been traditionally measured with timed, high-rate, discharge tests. Such tests have many disadvantages, however. They require heavy and cumbersome equipment, cause dangerous sparking, give imprecise results, and leave the battery in a significantly worse condition than existed before the test was performed. In response to the need for a better method, Champlin pioneered a testing technique based upon single-frequency ac conductance measurements. Various aspects of this well-accepted methodology have been disclosed in U.S. Patents **3,873,911**, **3,909,708**, **4,816,768**, **4,825,170**, **4,881,038**, **4,912,416**, **5,572,136**, **5,585,728**, **5,598,098**, and **5,821,756**.

With lead-acid batteries, **SOC** has been traditionally evaluated by observing the battery's open-circuit voltage or the specific gravity of its electrolyte. However, neither of these quantities provides information about the battery's **TSC, ASC, ACC, FCCC,** or **SOH**. Furthermore, specific gravity measurements are messy and impossible to perform on sealed cells. Moreover, open-circuit voltage cannot be measured under load conditions and, at any rate, is imprecisely related to **SOC** because both "surface charge" and temperature affect it.

Because of these drawbacks, several techniques for correcting voltage of lead-acid batteries to obtain **SOC** have been proposed. These include techniques

described by Christianson et al. in U.S. Patent **3,946,299,** by Reni et al. in U.S. Patent **5,352,968,** and by Hirzel in U.S. Patent **5,381,096.** However, such voltage correction methods are not very accurate. Furthermore, they are of little help with electrochemical systems other than lead-acid in which voltage may bear little relationship to **SOC.**

Due to these and other problems, techniques based upon ac or time-varying signals have been proposed for determining **SOC.** For example, Latner claims to determine **SOC** of NiCd batteries from ac bridge measurements of farad capacitance in U.S. Patent **3,562,634.** U.S. Patent **3,984,762** to Dowgiallo purports to determine **SOC** from the phase angle of the complex impedance at a single frequency. In U.S. Patent **4,743,855,** Randin et al. assert that **SOC** can be determined from the argument (i.e., phase angle) of the difference between complex impedances measured at two different frequencies. Bounaga, in U.S. Patent **5,650,937,** reportedly determines **SOC** from measurements of the imaginary part of the complex impedance at a single frequency. Basell et al. purport to determine **SOC** from the rate of change of impedance with frequency in U.S. Patent **5,717,336.** Ding et al., in U.S. Patent **6,094,033,** broadly assert that **SOC** can be determined from a battery's "impedance response, which can include series and parallel equivalent circuit parameters, i.e., resistance, capacitance, and phase angle, among others". Finally, techniques purporting to determine **SOC** from the transient response to an applied pulsed voltage and/or

current are disclosed by Andrieu and Poignant in U. S. Patent **5,530,361** and by Simon in French Patent Application **FR 2,749,396A.** The fact that none of these methods has gained wide acceptance, however, suggests that they may not be altogether satisfactory methods for determining **SOC.**

SUMMARY OF THE INVENTION

Testing apparatus senses the time-varying electrical response of an electrochemical cell/battery to time-varying electrical excitation. The cell/battery may, or may not, be in service. Computation circuitry responsive to the time-varying electrical response evaluates elements of a unique circuit model representation of the cell/battery. Performance parameters and physical parameters are computed from these element values. Computed performance parameters include, but are not limited to, "total storage capacity", "absolute stored charge", "state-of-charge", "absolute cranking current", "fully charged cranking current", and "state-of-health". Computed physical parameters include, but are not limited to, "exchange current", "maximum exchange current", "charge transfer conductance", "maximum charge transfer conductance", "double layer capacitance", and "maximum double layer capacitance". Computed parameters are either displayed to the user, employed to initiate an alarm, or used to control a process such as charging the cell/battery.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a block diagram of apparatus for evaluating performance parameters and physical

parameters of an electrochemical cell or battery in accordance with one embodiment of the present invention.

FIG. **2** depicts a generic **2n**-element small signal circuit model representation of an electrochemical cell or battery employed in the present invention.

FIG. **3** depicts the six-element small signal circuit model representation of a particular fully charged **12V VRLA** battery determined from complex immittance measurements at **5** Hz, **50** Hz, and **500** Hz.

FIG. **4** is a plot of the variation of the three subcircuit time-constants defined in FIG. **3** as charge is removed from the battery.

FIG. **5** is a plot of values of the three conductances defined in FIG. **3** as charge is removed from the battery.

FIG. **6** is plot of values of capacitances **C2** and **C3** defined in FIG. **3** as charge is removed from the battery.

FIG. **7** is a plot of the "exchange current" i_0 derived from "charge transfer conductance" **G3** of FIG. **5** as charge is removed from the battery.

FIG. **8** is a plot of the "state-of-charge" **SOC** derived from "charge transfer conductance" **G3** of FIG. **5** and "double layer capacitance" **C2** of FIG. **6** as charge is removed from the battery.

FIG. **9** is a plot of the "absolute stored charge" **ASC** determined from "double layer capacitance" **C2** of FIG. **6** as charge is removed from the battery.

FIG. **10** is a plot of the "total storage capacity" **TSC** derived from "charge transfer conductance" **G3** of FIG. **5** and "double layer capacitance" **C2** of FIG. **6** as charge is removed from the battery.

FIG. **11** is a plot of the "absolute cranking current" **ACC** derived from series conductance $G1 = 1/R1$ of FIG. **5** as charge is removed from the battery.

FIG. **12** is a plot of the function used to correct the "absolute cranking current" **ACC** for "state-of-charge" **SOC** to obtain the "fully charged cranking current" **FCCC** of FIG **13**.

FIG. **13** is a plot of the corrected "fully charged cranking current" **FCCC** as charge is removed from the battery.

FIG. **14** is a diagram of the "commonly accepted" circuit model showing the placement of a "charge transfer resistance" and "double layer capacitance" in <u>parallel</u> with one another.

FIG. **15** is a diagram of the $n = 3$ circuit model according to the present invention showing the placement of the "charge transfer conductance" and the "double layer capacitance" in two separate **G-C** subcircuits that are actually in <u>series</u> with one another.

FIG. **16** is a block diagram of apparatus for evaluating performance and physical parameters of an electrochemical cell or battery wherein an external source produces time-varying electrical excitation.

<u>DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS</u>

Method and apparatus for quickly and accurately determining performance parameters and physical parameters that does not discharge the battery, does not require the battery to be fully charged, and

5   tests batteries while "on line" would be of great value. The present invention addresses this need. It is based upon teachings disclosed by Champlin in U.S. Patents **6,002,238, 6,037,777, 6,172,483, 6,222,369, 6,262,563, 6,313,607,** and U.S. Patent Applications **60/299,876** and

10   **09/940,684,** all of which are incorporated herein by reference.

FIG. **1** discloses a block diagram of apparatus **5** for evaluating performance parameters and/or physical parameters according to one embodiment of the present

15   invention. Measuring circuitry **10** electrically couples to cell/battery **20** at positive terminal **15** and negative terminal **25** by means of current-carrying contacts **A** and **B** and voltage-sensing contacts **C** and **D**. Cell/battery **20** may, or may not, be in service. Under control of

20   microcontroller circuitry **30** via control path **35,** measuring circuitry **10** passes periodic time-varying excitation current **i(t)** through contacts **A** and **B** and senses periodic time-varying response voltage **v(t)** across contacts **C** and **D**. Amplification and analog to

25   digital conversion circuitry contained within measuring circuitry **10** formulates digital representations of **i(t)** and **v(t)** samples and communicates them to microcontroller circuitry **30** via data path **40.**

By appropriately processing these digital

30   representations, microcontroller circuitry **30** computes

real and imaginary parts of complex immittance --
either impedance Z or admittance Y -- at a measuring
frequency f_k; where f_k is a discrete frequency
contained in the periodic waveforms of $i(t)$ and $v(t)$.

5   Microcontroller circuitry **30** commands measuring
circuitry **10** to repeat these measurements at each one
of **n** discrete measuring frequencies, where **n** is an
integer number equal to or greater than **3**. This action
defines **2n** experimental quantities: the values of the **n**

10 real parts and the **n** imaginary parts of complex
immittance at each of the **n** measuring frequencies.
Microcontroller circuitry **30** then employs algorithms
disclosed in U. S. Patents **6,037,777** and **6,222,369** to
numerically combine the **2n** experimental quantities to

15 evaluate the **2n** elements of the circuit model
representation of the cell/battery disclosed in FIG. **2**.
This unique circuit model comprises a single series **R-L**
subcircuit in series with a plurality, **n-1**, of parallel
G-C subcircuits.

20   Microcontroller circuitry **30** computes one or
more performance and/or physical parameters of
cell/battery **20** from values of one or more elements of
this circuit model representation of FIG. **2**.
Additionally, microcontroller circuitry **30** can compare

25 one or more computed parameters with battery rating
information inputted by a user on input device **45** to
determine the battery's "state-of-health" **SOH**.
Finally, microcontroller circuitry **30** can output
appropriate performance or physical parameters to a

30 user on display **50,** and/or apply one or more computed

parameters to initiate an alarm **55** or to control a process **60** such as charging of the battery.

FIG. **3** discloses the six-element circuit model of a fully charged **12V** battery as determined with the apparatus of FIG. **1** using **n = 3**. The experimental battery was a **VRLA** (valve-regulated lead-acid) automotive battery of spiral-grid construction that was rated **700** CCA, **95** minutes reserve capacity, and **50** Ah capacity @ **20** hour rate. The three measurement frequencies were **5, 50,** and **500** Hz.

One notes from FIG. **3** that the **n = 3** circuit model comprises three two-element subcircuits in series:

- A series **R1-L1** subcircuit.

- A parallel **G2-C2** subcircuit.

- A parallel **G3-C3** subcircuit.

One notes further that the three subcircuits are characterized by three very different time constants. The shortest time constant, $\tau_1 = L1/R1 = 215.4\mu S$, belongs to the series **R1-L1** subcircuit. The next longest time constant, $\tau_2 = C2/G2 = 3.33mS$, belongs to the parallel **G2-C2** subcircuit; and the longest time-constant, $\tau_3 = C3/G3 = 51.3mS$, belongs to the parallel **G3-C3** subcircuit. Accordingly, the three subcircuits represent quite different physical processes that can be differentiated from one another by their time constants.

By analyzing similar three-frequency measurements on many lead-acid batteries, a consistent physical interpretation of the circuit model of FIG. **3**

has emerged. The theoretical basis for this interpretation can be found in the paper by Champlin and Bertness, "Results of Discrete Frequency Immittance Spectroscopy (DFIS) Measurements of Lead Acid Batteries", Proceedings of the 23rd International Telecommunications Energy Conference (INTELEC), Edinburgh Scotland, paper **53**, (October 2001).

According to this interpretation, series resistance **R1** represents the current-induced drop in electric potential across the metal connectors, plates, separators, active material, and electrolyte – with the majority of **R1** associated with the active material and electrolyte. Accordingly, conductance **G1 = 1/R1** correlates directly with high-rate load-test current such as cold-cranking amps (**CCA**). Series inductance **L1** describes energy storage in the battery's surrounding magnetic field, with no electrochemical component to **L1** yet observed.

Both the parallel **G2 − C2** subcircuit and the parallel **G3 − C3** subcircuit are believed to be linearized representations of nonlinear electrochemical processes occurring at the negative electrode surfaces. These two subcircuits together describe the response of negative electrode surfaces to changes in an externally applied electrochemical overpotential.

Electrochemical overpotential at an electrode surface consists of two parts: an *electrical* overpotential and a *chemical* overpotential. The *electrical* part arises from electrical forces on charged particles, and the chemical part arises from

concentration differences. The faster **G2–C2** subcircuit responds to the *electrical* part of an electrochemical overpotential and the slower **G3–C3** subcircuit responds to the *chemical* part. These two subcircuits add in *series* in the circuit model of FIG. **3** because the *electrical* overpotential and the *chemical* overpotential add together to form the *electrochemical* overpotential. Voltages (potentials) add in series.

FIGS. **4, 5,** and **6** display the results of three-frequency immittance measurements performed on the battery whose model is depicted in FIG. **3** during a discharge sequence. The battery was initially charged, allowed to reach equilibrium, and was then repeatedly discharged at an approximate **8**-hr rate in increments of approximately **3** ampere-hours. The battery was permitted to rest for **2.5** hours after each discharge period before the three-frequency immittance measurements were taken.

FIG. **4** is a plot of the variation of the three time constants defined in FIG. **3** as charge is removed from the battery. One notes that the time constants remain widely separated as charge is removed, and that the longest of the three, τ_3, is nearly independent of state-of-charge.

FIG. **5** discloses the variation of the three conductances, **G1 = 1/R1, G2,** and **G3** as charge is removed from the battery. Of particular interest is the fact that **G3** becomes small near full charge as well as near full discharge. This remarkable behavior sets **G3** apart from **G1** and **G2,** both of which reach

maxima at full charge. Such unusual behavior can be explained by assuming that **G3** describes *faradaic* processes occurring at the negative electrode surfaces and considering the kinetics of such processes.

5   The Butler-Volmer equation for faradaic processes at the negative electrode surfaces can be written:

$$i = i_f - i_b = i_0 \left(e^{\alpha n f V_3} - e^{-\left(1-\alpha\right)n f V_3} \right) \qquad (1)$$

10   In equation **(1)**, **i** is the current in the external circuit (assumed positive in the "charge" direction) while i_f and i_b are "forward" and "backward" ionic "reaction" currents, respectively, in the electrolyte. Physical parameter i_0 is the "exchange current"; α is
15   a "charge transfer coefficient" (less than unity); **n** is the number of electrons transferred per molecule reactant (two); and $f = (F/RT)$, with **F** being Faraday's constant, **R** the universal gas constant, and **T** the absolute (Kelvin) temperature. Voltage V_3 in equation
20   **(1)** is believed to be the *chemical* component of the *electrochemical overpotential* (positive for "charge" and negative for "discharge") at the negative electrode surfaces.

     The *chemical overpotential*, V_3, drives the
25   two ionic reaction currents. Under charging conditions ($V_3 > 0$), the <u>forward</u> ionic current, $i_f = i_0 \exp(\alpha n f V_3)$, is larger than i_0; while the <u>backward</u> ionic current,

$i_b = i_0 \exp(-\{1-\alpha\}nfV_3)$ is less than i_0. Accordingly, their difference yields a <u>positive</u> ("charging") current in the external circuit. Under discharging conditions ($V_3 < 0$), the opposite is true. In equilibrium ($V_3 = 0$), both forward and backward ionic currents are equal to the exchange current i_0, and the current in the external circuit is zero. Note that even with $i = 0$, there are still two equal ionic "exchange currents" flowing in opposite directions on the electrolyte side of the electrode/electrolyte interface.

For small variations in V_3, the equilibrium small-signal faradaic conductance, or "charge transfer conductance", follows by differentiating equation (1) with respect to $(N_C V_3)$, where N_C is the number of battery cells in series, and evaluating this derivative at $V_3 = 0$. The result is

$$G3 = \left.\frac{di}{d(N_C V_3)}\right|_{V_3 = 0} = \frac{nfi_0}{N_C} = (nF/N_C RT) \cdot i_0 \qquad (2)$$

One sees that at any given temperature, the "charge transfer conductance" G3 is proportional to the "exchange current" i_0. The "charge transfer conductance" and electrode "exchange current" are both physical parameters of great importance.

Equation (2) can be inverted to yield the "exchange current" i_0 in terms of "charge transfer

conductance" **G3**. For a **12V** (**6-cell**) battery at room temperature (**T = 293° K**), equation (**2**) yields

$$i_0 = \left(N_C RT/nF\right)\cdot G3 = \left(.07574\right)\cdot G3 \quad \textbf{amperes} \quad (3)$$

5

Fig. **7** displays i_0 calculated from equation (**3**) using the experimental **G3** data of Fig. **5**. One sees that i_0 approaches zero at both full charge and full discharge and reaches a maximum value of $i_{0\,max} = 27.5$ amperes at

10 approximately **50%** state-of-charge.

The remarkable variation of **G3** disclosed in FIG. **5** can now be explained. As the battery approaches full charge, the forward, or "charge", component of reaction current goes to zero because the number of

15 reaction sites available for the charge reaction (**PbSO₄** sites) approaches zero. Since forward and backward ionic currents are equal in equilibrium, the equilibrium backward current likewise goes to zero. Similarly, as the battery approaches full discharge,

20 the backward, or "discharge", component of reaction current goes to zero because the number of sites available for the discharge reaction (**Pb** sites) approaches zero. Again, since forward and backward ionic currents are equal in equilibrium, the

25 equilibrium forward current likewise goes to zero. Accordingly, the "exchange current" i_0 goes to zero in both cases. From equation (**2**), the "charge transfer conductance" **G3** -- which is simply proportional to i_0

-- likewise approaches zero at full charge and at full discharge, reaching maximum at **50%** state-of-charge.

By reasoning in accordance with this mechanism, one can write "charge transfer conductance" **G3** as -

$$G3 = 4 \cdot G3_{max} \cdot (N_{Pb}^{-}/N^{-}) \cdot (N_{PbSO_4}^{-}/N^{-}) \qquad (4)$$

where $N^{-} = N_{Pb}^{-} + N_{PbSO_4}^{-}$ is the total number of negative-electrode reaction sites, N_{Pb}^{-} is the number of such sites occupied by **Pb** molecules, and $N_{PbSO_4}^{-}$ is the number occupied by **PbSO$_4$** molecules. The factor **4** in equation **(4)** arises because **G3** equals **G3$_{max}$** when $N_{Pb}^{-} = N_{PbSO_4}^{-} = N^{-}/2$.

I now define the performance parameter "state-of-charge" **SOC** as the *fraction* of negative-electrode reaction sites occupied by **Pb** molecules. That is,

$$SOC \equiv (N_{Pb}^{-}/N^{-}) = 1 - (N_{PbSO_4}^{-}/N^{-}) \qquad (5)$$

Equation **(4)** can therefore be written

$$G3 = 4 \cdot G3_{max} \cdot (SOC) \cdot (1 - SOC) \qquad (6)$$

which obviously approaches zero when **SOC** approaches unity as well as zero.

FIG. **6** discloses the variation of capacitance **C2** and capacitance **C3** as charge is removed from the battery. Capacitance **C3** is seen to mimic the behavior of "charge transfer conductance" **G3** over the complete

5 range of Ah removed. This variation can be understood by noting that $C3 = \tau_3 \cdot G3$, and that τ_3 varies little as charge is removed (see FIG. **4**). Time constant τ_3 is believed closely related to the *reaction time* of *faradaic* processes at the negative electrode surfaces

10 (See U.S. Patents **6,137,269** and **6,294,697**).

Capacitance **C2** in FIG. **6** is observed to vary in an entirely different manner from **C3** as charge is removed. Instead of increasing and then decreasing, **C2** assumes its largest value with zero amp-hours

15 removed and simply decreases monotonically as charge is removed from the battery. Such behavior suggests that the **G2-C2** subcircuit is responsive to the *nonfaradaic* or *electrical* component of an *electrochemical* *overpotential* at the negative-electrode surfaces. In

20 this interpretation, capacitance **C2** represents the negative-electrode's *ionic* "double layer capacitance" — a physical parameter of considerable interest.

An ionic double layer can only form on metallic **Pb** molecules. It cannot form on

25 nonconducting **PbSO4** molecules. It follows that **C2** is proportional to N_{Pb}^-, the total number of reaction sites that are occupied by **Pb** molecules. Accordingly, "double layer capacitance" **C2** can be written

$$C2 = C2_{100} \cdot \left(N_{Pb}^{-}/N^{-}\right) = C2_{100} \cdot SOC \qquad (7)$$

where $C2_{100}$ is "maximum double layer capacitance" -- the value that would occur at **100%** state-of-charge.

Equation **(7)** indicates that physical parameter $C2_{100}$ relates to battery size and condition by being proportional to N^{-}, the total number of reaction sites available for charge/discharge reactions. Similarly, equation **(4)** indicates that physical parameter $G3_{max}$ relates to size and condition by being proportional to $(N^{-})^{2}$. Accordingly, I define the following useful quantity:

$$\xi \equiv \frac{(C2_{100})^{2}}{4 \cdot G3_{max}} \qquad (8)$$

which, for any particular class of cell/battery, is independent of battery size, condition and "state-of-charge". I have found that $\xi \cong 1.368 \cdot 10^{-2}$ for batteries of the type under consideration herein.

Equations **(6)**, **(7)**, and **(8)** can be combined algebraically to provide separate expressions for **SOC**, $C2_{100}$, and $G3_{max}$ in terms of ξ, **C2**, and **G3**. The results are-

$$SOC = \frac{1}{1 + \xi \cdot (G3/C2^{2})} \qquad (9)$$

$$C2_{100} = C2 + \xi \cdot (G3/C2) \tag{10}$$

and

$$G3_{max} = \frac{\{C2 + \xi \cdot (G3/C2)\}^2}{4 \cdot \xi} \tag{11}$$

5   By combining equation **(3)** and equation **(11)**, "maximum exchange current" $i_{0\,max}$ can be written as –

$$i_{0\,max} = \frac{\{N_C RT/nF\} \cdot \{C2 + \xi \cdot (G3/C2)\}^2}{4 \cdot \xi} \tag{12}$$

10   This physical parameter is of considerable theoretical interest since it describes the level of maximum chemical activity at the electrode/electrolyte interface.

FIG. **8** displays performance parameter **SOC**
15   (in percent) calculated from equation **(9)** by using the experimental **G3** and **C2** data disclosed in FIGS. **5** and **6**. Note that combining **G3** and **C2** data to determine **SOC** resolves the multi-value ambiguity of equation **(6)**. The "state-of-charge" determined in this manner
20   varies from a maximum value of **93.6%**, with zero ampere-hours removed from the battery, to a minimum value of **4.1%** with **45.2** ampere-hours removed. The observed, nearly linear, variation of **SOC** with ampere-hours removed provides excellent corroboration of the theory.
25   The performance parameters "absolute stored charge" **ASC** and "total storage capacity" **TSC** are

proportional to **C2** and $\mathbf{C2_{100}}$, respectively. Accordingly, I write –

$$ASC = K_{cs} \cdot C2 \tag{13}$$

5

and, from equation **(10)** –

$$TSC = K_{cs} \cdot \left\{ C2 + \xi \cdot (G3/C2) \right\} \tag{14}$$

10 where $\mathbf{K_{cs}}$ is a "charge storage" constant that depends upon the battery type, and upon the units of charge storage (i.e., ampere-hours @ an **8** hr rate, ampere-hours @ a **20** hr rate, reserve capacity minutes, coulombs, etc.) I find that for batteries of the type
15 under consideration herein, and with **ASC** and **TSC** expressed in ampere-hours @ an **8** hr rate, $\mathbf{K_{cs} \cong 11.3}$.

Taking the ratio of equation **(13)** to equation **(14)** shows that –

20
$$\frac{ASC}{TSC} = \frac{C2}{C2 + \xi \cdot (G3/C2)} = \frac{1}{1 + \xi \cdot (G3/C2^2)} = SOC \tag{15}$$

Thus, the performance parameter "state-of-charge" **SOC**, that is defined physically in terms of numbers of reaction sites by equation **(5)**, is actually the ratio
25 of the two performance parameters "absolute stored charge" **ASC** and "total storage capacity" **TSC** .

FIG. **9** displays performance parameter "absolute stored charge" **ASC** (in ampere-hours)

calculated from equation **(13)** using the experimental **C2** data disclosed in FIG. **6**. The "absolute stored charge" determined in this manner varies from a maximum value of **47.2** ampere-hours, with zero ampere-hours removed from the battery, to a minimum value of **1.9** ampere-hours with **45.2** ampere-hours removed. Note that "absolute stored charge" **ASC** decreases as the battery discharges - much like the level of liquid in a fuel tank. Accordingly, **ASC** would comprise an excellent "electric fuel gauge" readout.

FIG. **10** displays the performance parameter "total storage capacity" **TSC** (in ampere-hours) calculated from equation **(14)** using the experimental **G3** and **C2** data disclosed in FIGS. **5** and **6**. Note that the observed **TSC** varies very little as the battery is discharged. Ideally, **TSC** would not vary at all. The small variations observed are believed caused by minor inaccuracies in the $n = 3$ model. Performing immittance measurements at four or five frequencies and then employing an eight- or ten-element circuit model in the analysis greatly reduces such variations.

Performance parameter "absolute cranking current" **ACC** has been found experimentally to be proportional to $G1 = 1/R1$. Thus -

$$ACC = K_{cc} \cdot G1 \qquad\qquad (16)$$

where K_{cc} is a "cranking current" coefficient that depends upon the type of battery and the definition of "cranking current". For batteries of the type under

consideration, and with "cranking current" defined to be SAE "cold cranking amperes", $K_{cc} \cong 2.7$. FIG. **11** displays performance parameter **ACC** determined from equation **(16)** by using the **G1** data of FIG. **5**. One sees that **ACC** decreases significantly as charge is removed from the battery.

For batteries that are less than fully charged, the performance parameter "fully charged cranking current" **FCCC** can be determined by correcting the **ACC** according to –

$$FCCC = ACC \cdot F(SOC) \tag{17}$$

where **F(SOC)** is a "correction factor" that depends upon "state-of-charge". FIG. **12** discloses an emperically determined **F(SOC)** for correcting the **ACC** of batteries of the type under consideration. This function can be expressed mathematically as –

$$F(SOC) = \frac{1}{1 - 0.5 \cdot (SOC - 1) - 1.0 \cdot (SOC - 1)^2 + 0.4 \cdot (SOC - 1)^3} \tag{18}$$

FIG. **13** displays performance parameter **FCCC** obtained by correcting the data of FIG. **11** according to equation **(17)** using the correction factor defined by equation **(18)** (FIG. **12**). One sees that the corrected **FCCC** varies by only **±2.7%** from **695** amperes over the entire range of discharge down to $SOC = 20\%$.

One determines the performance parameter "state-of-health" **SOH** by either of two methods. The first method is to compare the computed "total storage capacity" **TSC** with an appropriate user-inputted capacity rating such as the battery's rated "ampere-hour capacity" or rated "reserve capacity" in minutes. The second method is to compare the computed "fully charged cranking current" **FCCC** with an appropriate user-inputted cranking rating such as the battery's rated "cold cranking amperes" (**CCA**). In either case, the battery is assumed to have "failed" the **SOH** test if the calculated parameter value is less than a predetermined fraction, say **75%**, of the rated parameter value. Either **SOH** method, or both methods, may be employed -- depending upon the type of service that the battery is expected to experience.

This completes the disclosure of my invention. FIGS. **14** and **15**, however, will serve to place the innovative nature of my invention in perspective. FIG. **14** illustrates the "commonly accepted" equivalent circuit model of a cell/battery at the present time. (See, e.g., U.S. Patent **6,167,349** to Alvarez. See also E. Karden, et al., "A method for measurement and interpretation of impedance spectra for industrial batteries", J Power Sources **85** (**2000**), pp. **72 - 78.**) The "commonly accepted" model, also known as the "Randles equivalent circuit", places a "charge transfer resistance" and a "double layer capacitance" in <u>parallel</u> with one another. In my opinion, this model is fundamentally wrong and cannot possibly lead

to correct evaluation of any of the performance parameters or physical parameters evaluated herein.

My measurements and analysis have shown that the "charge transfer conductance" (the reciprocal of "charge transfer resistance") and the "double layer capacitance" are elements of two separate **G-C** subcircuits that are actually in <u>series</u> with one another in the correct circuit model (see FIG. **15**). Furthermore, the "double layer capacitance" of the correct model varies directly with the number of reaction sites available for the discharge reaction (equation **(7)**); while the "charge transfer conductance" of the correct model varies directly with both the number of sites available for the discharge reaction and also the number available for the charge reaction (equation **(4)**). These important new discoveries set my work totally apart from all of the prior art.

To summarize, I have herein disclosed new methods and apparatus for evaluating the following six performance parameters:

1. "Absolute stored charge" **ASC** (equation **(13)**).
2. "Total storage capacity" **TSC** (equation **(14)**).
3. "State-of-charge" $\mathbf{SOC = ASC/TSC}$ (equation **(9)**).
4. "Absolute cranking current" **ACC** (equation **(16)**).
5. "Fully Charged Cranking Current" **FCCC** (equation **(17)**).
6. "State-Of-Health" **SOH**.

Furthermore, in the course of this disclosure I have also revealed new methods and apparatus for evaluating the following six important physical parameters:

1. "Exchange current" i_0 (equation **(3)**).

2. "Maximum exchange current" $i_{0\,max}$ (equation **(12)**).

3. "Charge transfer conductance" **G3**.

4. "Maximum charge transfer conductance" $G3_{max}$ (equation **(11)**).

5. "Double layer capacitance" **C2**.

6. "Maximum double layer capacitance" $C2_{100}$ (equation **(10)**).

My invention, however, is not limited to evaluating only these twelve parameters.

Although my disclosure has referred to particular apparatus and algorithms previously disclosed in U.S. Patents **6,002,238**, **6,037,777**, **6,172,483**, **6,222,369**, and **6,262,563**, other methods will be apparent to those skilled in the art. For example, one could evaluate elements of the correct circuit model by using pulsed or stepped excitation such as that described in U.S. Patent **6,118,275** to Yoon or in U.S. Patent **6,167,349** to Alvarez; or by using random or pseudo-random excitation such as that described in PCT Application **WO 99/18448** to Scott. One could also employ bridges, frequency response analyzers, or other types of ac instrumentation to measure complex admittance or complex impedance at multiple frequencies. The range of measurement frequencies is unrestricted and could

include frequencies in the millihertz and microhertz region (**f<1**) as well as frequencies in the range of hertz (**f>1**).

The embodiment disclosed in FIG. **1** utilizes time-varying electrical excitation **i(t)** generated internally to apparatus **5** by internal measuring circuitry **10**. Alternatively however, the requisite time-varying electrical excitation could be developed by an external source **65** as disclosed in FIG. **16**. Such an external source could simply comprise normal "noise" currents flowing through a cell/battery during service, such as taught in PCT Application **WO 93/22666** to Robinson. It could also comprise "ripple" signals arising from an unfiltered battery charger during bench-charging of the cell/battery or charging by an alternator in a vehicle. Although, time-varying current **i(t)** has been presented as an electrical excitation and time-varying voltage **v(t)** as an electrical response, the roles of **i(t)** and **v(t)** could be reversed. Time-varying voltage **v(t)** could be the electrical excitation and time-varying current **i(t)** the electrical response. All such modifications and variations are included in my invention.

It is well known that elements of any circuit model can be readily subdivided and rearranged to obtain a derivative circuit that appears to be quite different, but is in effect electrically equivalent to the original circuit. My invention includes all such derivative circuits that are electrically equivalent to the models of FIG. **2** and/or FIG. **3**. One could use a

circuit model containing, e.g., eight or ten elements rather than the six elements treated herein. This straightforward modification is likewise included in my invention.

5   Instead of the algorithms disclosed in U.S. Patents **6,037,777** and **6,222,369** to evaluate elements of the circuit model, one could simply employ a conventional "complex least-squares curve fitting" procedure. If accuracy is not essential, one could

10   even take advantage of the fact that the time constants are widely separated from one another and simply assume that the subcircuits are not coupled. Thus, with some batteries, it may be possible to obtain a reasonably accurate circuit model from a very simple computational

15   analysis of measured time-varying electrical response.

The invention is not limited to the particular circuitry implementations disclosed herein. Measuring circuitry, electrical excitation circuitry, electrical response sensing circuitry, computational

20   circuitry, etc., can be implemented in hardware, software, or combinations thereof. Such circuitry can share common elements or be implemented with common components such as a common microprocessor, microcontroller, or personal computer. Workers skilled

25   in the art will recognize that these and other variations may be made in form and detail without departing from the true spirit and scope of my invention.